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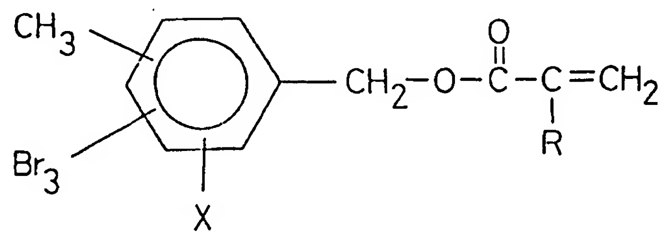
(71) Applicants
Dynamit Nobel Aktiengesellschaft
521 Troisdorf,
bez Köln,
Postfach 1209,
Germany
(72) Inventors
Werner Schmidt
Egon-Norbert Petersen
Norbert Vollkommer
(74) Agents
Haseltine Lake & Co

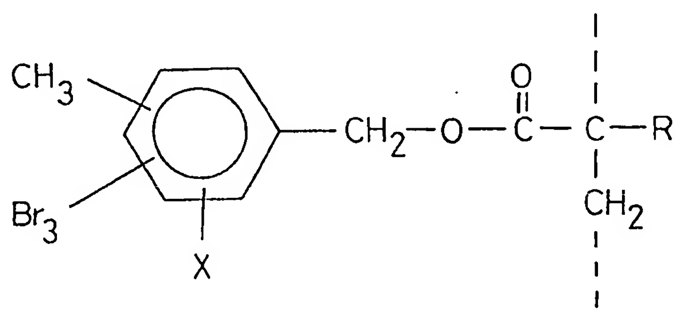
(54) Methyltetrahalobenzylacrylates and methacrylates, and polymers and plastics compositions based thereon

(57) Novel esters having the general formula:



(I)

wherein R is hydrogen or methyl, and X is bromine or chlorine, are prepared by esterifying the corresponding halide. Polymers prepared from said esters and thus containing structural units of the formula:



(III)

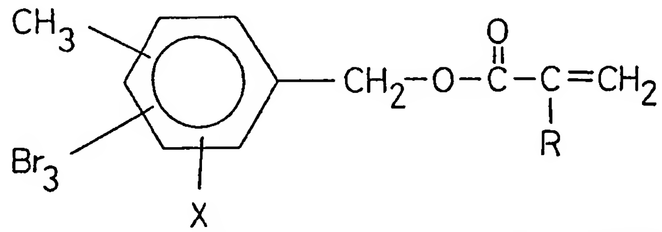
are useful as flameproofing agents in plastics compositions.

SPECIFICATION

Methyltetrahalobenzylacrylates and methacrylates, and polymers and plastics compositions based thereon

This invention relates to methyltetrahalobenzylacrylates and methacrylates, polymers produced therefrom and the use of such polymers as flameproofing agents for polymeric materials.

According to one aspect of the present invention there is provided an ester having the general formula

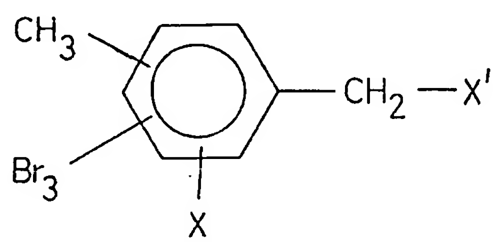


(I)

in which R represents a hydrogen atom or a methyl group, and X represents bromine or chlorine.

The atom X is preferably bromine, although it may instead be chlorine. When chlorine is present in the molecule it is preferred that on average the nucleus carries up to 0.3 chlorine atoms, and more preferably only up to 0.1 chlorine atoms.

According to another aspect of the invention there is provided a process for producing such esters which comprises reacting a halide of general formula



(II)

in which X′ represents a halogen atom, with an alkali metal salt of acrylic and/or methacrylic acid, to form the desired ester.

The atom X′ is preferably a bromine atom, i.e. the halide is a bromide. When chlorides are used as starting material, halogen exchange may lead to the chlorine subsitution on the nucleus which is mentioned above.

In accordance with the process, the halide can be converted to the ester with the stoichiometrically required quantity of salt. Preferably, however, a stoichiometric excess of salt is used, for example an excess of up to 10 mol %, and more preferably up to 5 mol %. The process is preferably carried out at a temperature of from 50 to 150°C, more preferably from 80 to 130°C.

It is preferred to carry out the process in the presence of a polymerisation inhibitor, for example up to 5% by weight of inhibitor, based on the acid which is used. Phenolic inhibitors such as hydroquinone, *p*-benzoquinone, pyrocatechol, 4-tert butylpyrocatechol, and hydroquinonemonomethylether have proved to be suitable for inhibiting polymeriation. Hydroquinone is particularly preferred.

The process is preferably performed in the presence of a polar organic solvent or a mixture thereof with water. The polar solvent may be, for example, an alcohol, preferably with 1 to 4 carbon atoms, a glycol, an ether alcohol, tetrahydrofuran, dioxane, dimethoxyethane, dimethylformamide, dimethylsulphoxide, dimethylacetamide, N-methylpyrrolidone or mixtures thereof. The use of ethyleneglycol monomethylether is preferred.

The acrylic or methacrylic acid salt may be prepared *in situ*, for example by reacting an alkali metal hydroxide, carbonate or alocholate, preferably sodium hydroxide, with acrylic and/or methacrylic acid. The salt formation between the acrylic and/or methacrylic acid and the alkali preferably takes place at a temperature of from 10 to 80°C, more preferably at room temperatre. For example the alkali may be added to the acid dissolved in the solvent, preferably in the form of an aqueous solution when hydroxides or carbonates are used. If required, the polymersation inhibitor may be present during ths salt formation stage.

In one embodiment of the process, after adding the methyltetrahalobenzylhalide, the temperature is raised to 50 to 150°C, more preferably 80 to 130°C, and the mixture is left to react practically until the conversion is complete. The reaction time is usually between 0.5 and 4 hours. The methyltetrahalobenzylbromides have been found to be usually more reactive than the chlorides.

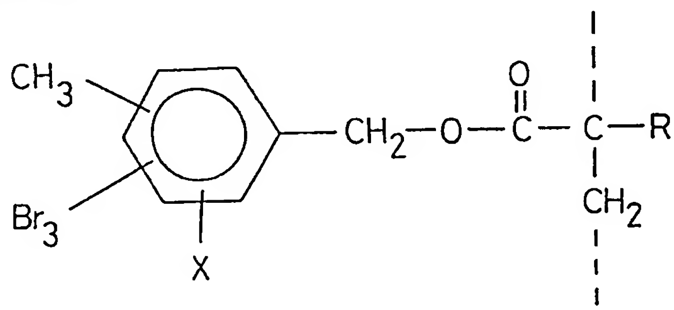
The progress of the reaction may be followed if required by quantitative analysis of the alkali bromide or chloride produced, for example by means of the determination according to Mohr.

It has been found that an excess of from 1 to 5 mol % of the alkali metal salt of the (meth)-acrylic acid compared with the methyltetrahalobenzylhalide is expedient for a substantially complete conversion, especially as the excess can be separated off from the product mixture, together with the alkali metal halide, after reaction has ceased.

It is also preferred that the alkali metal salt solution contains a very small stoichiometric excess, for example of up to 5 mol %, and preferably up to 3 mol % of, the acid.

After the reaction has ceased the precipitated alkali metal halides, together with any small amounts of acrylic and/or methacrylic acid esters which may have been polymerised, may be separated from the dissolved esters, for example by filtration or centrifuging. The esters of formula (I) may then be obtained from the solution in crystalline form, for example by cooling the filtrate; and alternatively they may be precipitated with water and dried, preferably at room temperature.

According to yet another aspect of the invention there is provided a polymer which contains structural units of general formula



(III)

in which R represents a hydrogen atom or a methyl group, and X represents bromine or chlorine.

Again, X may be bromine or chlorine, and, when chlorine, the nucleus preferably carries on average up to 0.3 chlorine atoms more preferably up to 0.1 chlorine atoms.

The polymer may be a homopolymer or a copolymer.

In accordance with the invention the polymer is produced by polymerising an ester of general formula (I), preferably in the presence of a radical former such as dicumyl peroxide, dibenzoyl peroxide or azodiisobutyronitrile. It is preferred to carry out the polymerisation at a temperature of from 0 to 150°C.

In the case where the polymer is a copolymer, it contains structural units other than those of general formula (III). For example these other units may be based on an ethylenically unsaturated monomer or an unsaturated polyester. In such case the polymerisation process is carried out in the presence of a monomer or polyester which is copolymerisable with the ester of general formula (I).

The polymerisation mechanism both for homopolymerisation and copolymerisation is preferably radical, although an anionic-initiated polymerisation has also proved successful. Organic or inorganic peroxides or aliphatic azo-compounds may be used as radical formers, the previously mentioned dicumylperoxide, dibenzoylperoxide and azodiisobutryonitrile being preferred. The radical formers may be thermally excited to the point of disintegration by means of energy-bearing radiation or by virtue of a redox reaction. Conventional polymerisation temperatures, generally in the region of 0°C to 150°C, are preferably used. Also possible is a polymerisation initiation by incident radiation, if necessary in the presence of sensitisors, or a thermal polymerisation initiation. In the case where polymerisation is anionically induced, it is preferred to use as initiators, the alkyl, alcoholate, amide and Grignard derivatives of alkali and alkaline earth metals.

As ethylenically unsaturated monomers which are capable of being copolymerised with the unsaturated esters of formula (I) there may be mentioned styrene, acrylic acid esters and methylacrylic acid esters, preferably those with 1 to 6 carbon atoms in the alcohol radical, unsubstituted and chlorine or bromine-substituted xylylenebisacrylates or bis methacrylates, acrylonitrile, butadiene and isoprene, as well as fumaric and maleic acid or ester forming derivatives thereof such as maleic anhydride. In this context the term copolymer is understood to include the case where the polymer includes two or more kinds of structural units. For example several comonomers may be polymerised to form a terpolymer.

Preferred monomers are styrene and acrylic and methacrylic acid esters, as well as ester(s) and polyester(s) of fumaric and maleic acid. In the case where the structural units of the polymer include derivatives of a polyester, the esters of the invention may be included as cross-linking components of preferably styrene-based solutions of unsaturated polyester resins based on diol-components such as ethyleneglycol or neopentylglycol and unsaturated acid components such as furmaric or maleic acid, optionally also including saturated dicarboxylic acid components. The unsaturated esters of formula (I) are thus included in the cross-linking copolymerisation of the fumaric or maleic ester double-bonds with the reactive solvent, preferably styrene.

The polymerisation of the esters of formula (I) according to the invention and the copolymerisation with the previously mentioned monomers or polyesters may be conducted substantially in solution or in suspension. Although the esters of formula (I) are generally in the form of firm crystalline substances at room temperature, it is possible to copolymerise them with liquid comonomers such as styrene, or acrylates or methacrylates by an emulsion polymerisation process.

The monomeric esters of formula (I) used in the polymerisation process may have been previously produced and isolated. It is, however, possible and indeed preferred to carry out the polymerisation of the unsaturated esters in the same vessel, or even in another vessel, without carrying out the intermediate stage of isolating the esters from the product mixture and purifying them. Accordingly, the production of the

monomeric esters and their polymerisation and/or copolymerisation given an addition of suitable comonomer, may be carried out in a continuous operation.

By way of example it has been found to be possible to produce polyacrylates or polymethacrylates including structural units of general formula (III) from methyletetrahalobenzylhalides by means of a single process in which the initial product mixture formed includes the monomeric ester in solution, to which is added a polymerisation initiator - if required, after diluting with more solvent - the solution then being brought to polymerisation temperature with the exclusion of air. It has been found that the other components of the initial product mixture do not inhibit the polymerisation reaction. The polymers produced by such continuous processes have been found to have the same properties as those polymers produced from isolated and purified esters of formula (I).

When unsaturated polyester resins (UP-resins) containing maleic and/or fumaric acid units are hardened, the maleic and/or fumaric double-bonds react with the double bonds of the cross-linker, usually styrene. In accordance with the invention, when the esters of formula (I) are present in the resin, their double bonds also take part in the cross linking. It has been found that by adding the unsaturated esters of formula (I) to the resin, valuable improvements in quality may be achieved, particularly with regard to the impact and notched impact strength and rigidity, whilst the resistance to heat is surprisingly maintained.

Preferably, in the case where the polymer is a copolymer, it contains from 10 to 20 % by weight, more preferably 15 to 20% by weight of structural units of formula (III), based on the polymer as a whole e.g. a hardened UP-resin.

The homopolymers and copolymers according to the invention are thermoplastic polymers. Contrary to expectation it has been found that the halogen content does not generally hinder polymerisation; on the contrary, high-polymer, uncrosslinked homopolymers, uncrosslinked copolymers and/or hardened UP-resins generally result which possess characteristics typical of high polymers such as high impact strength, resistance to tearing and high Vicat- and/or Martens-temperatures. Surprisingly the polymers generally have an unusually high thermal stability, so that it is usually possible to process them without substantial discolouration or disintegration at the treatment temperatures conventionally used for thermoplasts. Further, it is possible to employ process temperatures which are greater than may be used with conventional polymers which are chemically similar.

It has been found that the polymers usually show an improved resistance to the contamination and disintegration caused by microorganisms, this being by virtue of their halogen content which cannot be lost by the insertion of bromine-containing esters into the macromolecules - which is not the case with the simple addition of bacteriostatically or fungistatically effective substances.

Thermoplastic polyesters, such as polyetheylene terephthalate and polybutylene terephthalate have recently been used on a wide scale. Polybutylene terephthalate in particular has acquired a considerable share of the market by virtue of its many favourable properties, such as its easy processibility and rapid crystallisability coupled with the high impact strength, hardness and precision of mouldings produced from it. By virtue of its favourable electrical properties, polybutylene terephthalate is also widely used in the electric industry.

Like most thermoplasts, however, thermoplastic polyesters are attended by the disadvantage that they are readily inflammable, with the result that in some cases their use is restricted if, indeed, they can be used at all. There has been no shortage of attempts to provide polyesters of the type in question with a fire-retarding finish. In fact, various substances are even commercially available as flameproofing additives for such polyesters. However, the requirements which a flameproofing agent has to satisfy are so numerous that, hitherto, the problem has never been satisfactorily solved. For example, a flameproofing agent suitable for polybutylene terephthalate (PBT) must not affect either the appearance or the physical and chemical properties of the polyester. It must not diffuse out of the compound and either evaporate (by virtue of its vapour pressure), in which case the flameproofing effect would be lost, or form a coating on the surface of the moulding, i.e. chalk out. Mouldings which are affected in this way are of reduced utility, particularly in the electrical industry. Another requirement which a suitable flameproofing agent should satisfy is that it should show adequate thermal stability so that it is capable without decomposing or giving to discolouration, of withstanding the high processing temperatures of the moulding compositions (from 240 to 300°C) and also the high temperatures to which the mouldings are subsequently exposed for prolonged periods in their practical application. Finally, the price of the flameproofing should not exceed certain limits.

Known flameproofing additives include, in particular, brominated diphenyls or diphenyl ethers and also many other bromine - or halogen-containing compounds. Almost all of these compounds chalk out, seriously affect the mechanical properties of PBT for example, and lead to brittleness, with the result that they can only be used to a limited extent for reinforced PBT, and are generally unsuitable for non-reinforced PBT.

It has surprisingly been found that the polymers of the invention have a flameproofing effect on such polyesters and on other polymeric materials without the above mentioned disadvantages. Accordingly, a still further aspect of the invention provides a plastics composition which comprises a polymeric material and, as flameproofing agent therefor, a polymer containing structural units of geneal formula (III) as defined hereinbefore. The plastics composition may be a physical admixture of the polymeric material and the flameproofing polymer.

It has been found that the homopolymers and copolymers generally show high thermal stability far

beyond that of known bromine-containing flameproofing agents, may be mixed in without decomposing at the processing temperatures of the polymeric material, e.g. a thermoplastic polyester, and may even be repeatedly thermoplastically processed to form moulding compositions without producing discolouration or other signs of decomposition. Further, the polymers have been found to impart excellent protection against fire and very good self-extinguishing properties.

The polymeric material which is incorporated in the composition may be a high-melting plastic or a plastic of the type which has to be processed at high temperatures. For example the polymeric material may be a thermoplastic high melting polyester such as polyethylene terephthalate or polybutylene terephthalate. The polymer flameproofing agents may also be used without decomposition or discolouration for other high-melting plastics processed at high temperatures or exposed to high temperatures in service, such as polyethers, polyacetals, polysulphones, polyimides, polycarbonates, polyphenylene sulphide or polyaryl esters.

In addition, the flameproofing polymers may generally be used for any plastics compositions to be provided with a fire-retarding finish, particularly when the maintenance of favourable material properties is an important factor, for example in polyolefins, such as polyethylene, polypropylene or polybutylene; in polyacrylates and polymethacrylates; in polyacrylonitrile; in polystyrene; and in copolymers and terpolymers thereof, such as copolymers and terpolymers of acrylonitrile or methacrylates together with butadiene and styrene.

In the case of the homopolymers, it is preferred that the halogen content of the flameproofing agents is from 40 to 65% by weight and, more preferably from 40 to 60% by weight. In the case of the copolymers, the halogen content is preferably from 20 to 45% by weight. Such copolymers may for example be used as, or as a component of, starting materials for plastics compositions. The nature of the plastics compositions of the invention is basically not limited. However, it is particularly preferred to add the flameproofing agents, which in some cases are themselves powder-form thermoplasts, to thermoplasts. As materials of comparable thermal stability, the new flameproofing agents have been found to be of particular value for high-melting plastics compositions or for plastics compositions which have to be processed at high temperature, particularly thermoplasts.

In a preferred embodiment the compositions of the invention contain from 5 to 20% by weight of the polymer, and more preferably from 7 to 12% by weight thereof. It is preferred, too, that the compositions additionally include a substance which acts synergistically with the flameproofing polymer, for example in an amount of from 2 to 12% by weight, and preferably from 4 to 7% by weight. The substance may be, for example, a compound of antimony or of boron, and is preferably antimony trioxide.

The plastics compositions of the invention may additionally contain a filler and/or a reinforcing material, preferably in a quantity of from 2 to 60% by weight and more preferably in a quantity of from 10 to 40% by weight. Preferred fillers and/or reinforcing materials are glass fibres of all kinds. For example glass fibres as fillers and/or reinforcing materials have been found to be of particular value for fire-retarding thermoplastic high-melting polyesters, particularly polybutylene terephthalate and polyethylene terephthalate.

All the percentage quantities indicated are based on the total quantity of the plastics composition on the plastic.

The flameproofing polymers, which are generally in the form of fine powders, may be incorporated into the composition by mixing them with the polymeric material, optionally together with synergists and other additives, in a suitable mixing vessel and subjecting the resulting mixture to thermoplastic processing. However, they may also be added during the polycondensation or polymerisation reaction without affecting the reaction itself.

In general, the flameproofing polymers have only a minimal effect on the mechanical properties of the polymeric materials flameproofed with them. For example it has been found that they have an excellent flameproofing effect on reinforced and non-reinforced PBT when added in quantities of only 6 to 12% by weight, and preferably 8 to 10% by weight, with a synergistically acting substance, such as Sb_2O_3 for example, as measured by the Underwriters Laboratories test (Subject 94), in which they achieved the highest possible rating (VO). At the same time, the mechanical properties of the plastics composition, for example the impact strength values measured in accordance with DIN 53 453, after flameproofing in accordance with the invention have been found to be no worse than those of untreated polymeric materials. Accordingly the flameproofing agents can be used very successfully not only in filled or reinforced PBT, but also in non-reinforced PBT, without critically affecting the mechanical properties.

The properties of other plastics compositions are also usually negligibly affected. The polymeric materials thus flameproofed, particularly high-melting plastics, are particularly suitable for use in the electrical industry, in the manufacture of electrical equipment, for example switch housings, in the insulation field and for similar applications, because the flameproofing agents are particularly compatible with PBT, and mouldings in which they are present have generally been found not to show signs of chalky deposits or excessive weight loss, even after storage for 28 days at 150°C. Particularly good results have also been obtained in reinforced or filled plastics compositions where flameproofing is known to be more difficult than in non-reinforced materials on account of the wick effect of the fillers and/or reinforcing materials.

The following Examples, in which, in context, the percentages quoted represent % by weight unless otherwise indicated, illustrate the invention.

Example 1 (production of ester)

75.6 g (105 mol) acrylic acid and 1 g hydroquinone were dissolved in 1200 ml ethyleneglycolmonomethylether in a three necked flask equipped with stirrer, dropping funnel and reflux cooler. A solution of 41.2 g (1.03 mol) NaOH dissolved in 40 ml water was added dropwise and with stirring to the solution in the vessel at room temperature. Subsequently, 501 g (1 mol) *p*-methyltetrabromobenzylbromide was introduced, the temperature was raised to 110°C and the reaction mixture was stirred for 2 hours at that temperature.

During the reaction to form the unsaturated ester a cloudiness resulted from the deposition of NaBr. A Mohr determination of the NaBr showed a 99% conversion after a reaction time of 2 hours. Undissolved material was removed from the hot product mixture by suction and the filtrate was cooled to +5°C. The acrylate of formula (I) where R=H crystallised out and was removed by suction, washed once with cold ethyleneglycolmonomethylether and then twice with water, and dried at room temperature in a vacuum over P_2O_5. Yield 396 g *p*-methyltetrabromobenzylacrylate (80% of the theoretical).

The analysis of the double-bond content according to Beesing indicated a purity of the acrylate of 98.2%.

Elemental analysis:

Calc.	C 26.8	H 1.6	O 6.5	Br 65.1
Found	C 26.9	H 1.8	O 6.3	Br 65.0

Example 2 (production of ester)

In a reaction vessel of the type described in Example 1 and under the same reaction conditions, 90.3 g (1.05 mol) methacrylic acid and 41.2g (1.03 mol) NaOH (as a 50 % aqueous solution) were reacted in 1000 ml ethyleneglycolmonomethylether as solvent and in the presence of 1 g hydroquinone, with 501 g (1 mol) *p*-methyltetrabromobenzylbromide.

After 2 hours at 110°C, 97% conversion was achieved, based on the bromide analysis according to Mohr. The quantity of the product was somewhat greater than that produced in Example 1.

The undissolved product and the NaBr were removed by suction whilst hot, and the solution was cooled to +5°C. The methacrylate of formuia (I) with $R=CH_3$ which crystallised out was removed by suction, washed once with cold ethyleneglycol monomethylether and subsequently twice with water, and dried at room temperature in a vacuum over P_2O_5.

Yield: 368 g *p*-methyltetrabromobenzylmethacrylate (73% of the theoretical)

Melting point: 113 - 116°C

Purity: 97.4% (calculated from the double-bond content)

Elemental analysis:

calc.	C 28.45	H 1.97	Br 63.24	O 6.34
found	C 28.7	H 2.0	Br 63.1	O 6.1

In a manner corresponding to that described in Examples 1 and 2, *o*-methyltetrabromobenzylbromide and *m*-methyltetrabromobenzyl bromide were converted with Na-acrylate and Na-methacrylate respectively to form the corresponding acrylate and methacrylate of formula (I).

Example 3 (Production and polymerisation)

76 g (1.05 mol) acrylic acid and 0.5 g hydroquinone were dissolved in 1100 ml ethyleneglycolmonomethylether in a reaction vessel equipped with stirrer, reflux cooler and dropping funnel. A solution of 41.3 g (1.03 mol) sodium hydroxide in 42 ml water was added in portions, with stirring. Subsequently 500.7 g (1 mol) *p*-methyltetrabromobenzylbromide was introduced and heated to the reaction temperature of 110°C. After 2 hours at 110°C the conversion, as indicated by the bromide analysis, was practically quantitative.

5 g Dicumylperoxide was added to the vessel as polymerisation initiator whilst passing a gentle flow of nitrogen therethrough and simultaneously raising the temperature to 125°C. The polymerisation reaction was continued for 5 hours at 125°C. The resultant polymer suspension was removed by suction after cooling the product mixture. The polymer was then washed once with methanol and twice with water, and dried at a temperature increasing to 150°C.

460 g poly-(*p*-methyltetrabromobenzyl)-acrylate was obtained as a white powder, corresponding to a yield of 93.5%. Its softening temperature (Kofler-block) was 240°C.

Elemental analysis:	calc. C 26.9	found C 26.6
	Br 65.3	Br 64.8

Weight loss: (thermogravimetric analysis; 8 degrees C/min in air)

1% at 286°C; 5% at 301°C; 10% at 312°C

Poly-(*o*-and/or *m*-methyltetrabromobenzyl)-acrylates were obtained in analagous manner by using *o*-and/or *m*-methyltetrabromobenzylchloride as the starting material.

Example 4 (production and polymerisation)

Under the reaction conditions of Example 3 a solution of the monomeric methacrylate of formula (I) with $R=CH_3$ in 1300 ml methylglycol was produced. The production was from 90.4 g (1.05 mol) methacrylic acid, 41.2 g (1.03 mol) sodium hydroxide dissolved in 40 ml water, and 501 g (1 mol) *p*-methyltetrabromobenzylchloride, the reaction being carried out in the presence of 0.8 g hydroquinone for

the prevention of premature polymerisation during the condensation reaction.

After passing a current of nitrogen over the reaction mixture 10.8 g (2%) of dicumylperoxide was added thereto as polymerisation initiator and polymerisation was carried out for 5 hours at the boiling temperature of the methylglycol. The resultant polymer dispersion was removed by suction after cooling and washed and dried as before.

481 g poly-(*p*-methyltetrabromobenzyl)-methacrylate was obtained as a white powder in a yield of 95.4%. Its softening temperature (Kofler-block) was 250°C.

	calc.	found
Elemental analysis:	C 28.5	C 28.7
	Br 63.5	Br 63.2

The polymer was insoluble in the solvent which was used, as well as being soluble in tetrahydrofuran, dimethylformamide, dimethylacetamide, *o*-dichlorobenzene, N-methylpyrrolidone and a phenol/*o*-dichlorobenzene mixture (60/40).

The poly-(*o*-and/or *m*-methyltetrabromobenzyl)--methacrylates were obtained in analogous manner by reacting *o*-and/or *m*-methyltetrabromobenzylbromide with sodium methacrylate.

Example 5 (copolymerisation)

200 g *p*-Methyltetrabromobenzylacrylate (≈0.41 mol) and 200 g methylmethacrylate (2.0 mol) were dissolved in 800 ml toluene. After adding 4 g (1%) azodiisobutyronitrile as polymerisation initiator, copolymerisation was carried out at 50°C for 30 hours in a nitrogen atmosphere. The resultant highly viscous solution was thinned with 400 ml toluene and the produce was precipitated with an excess of methanol. After washing out with methanol and drying, 360 g of copolymer was obtained as a white powder. The yield was 90%, in relation to the monomer mixture, and had a bromine-content of 30.8%.

Physical properties of the copolymer were as follows:

Softening temperature:	160°C (Kofler-block)
Vicat-temperature:	108°C
Martens-temperature:	86°C
Impact strength	11.6 KJ/m^2
Notched impact strength:	2.9 KJ/m^2
U.L. test:	VO

Example 6 (copolymerisation)

A copolymer was produced from 80 g (0.163 mol) *p*-methyltetrabromobenzylacrylate and 320 g (3.2 mol) methylmethacrylate according to the procedure in Example 5.

Yield: 370 g (92.5%)

Br-content: 10.7%

Softening temperature:	145°C (Kofler-block)
Vicat-temperature:	97°C
Martens-temperature:	77°C
Impact strength:	9.5 KJ/m^2

Examples 7 and 8 (copolymerisation)

According to the procedure of Example 5, a copolymer was produced (Example 7) from 200 g (0.396 mol) *p*-methyltetrabromobenzylmethacrylate and 200 g methylmethacrylate (2.0 mol). In Example 8 the polymer was produced from 80 g (0.159 mol) *p*-methyltetrabromobenzylmethacrylate and 320 g (3.2 mol) methylmethacrylate.

	Example 7	Example 8
Yield:	320 g	350 g
	≈80%	≈87.5%
Bromine content:	34.5%	11.4%
Softening temperature: (Kofler-block)	180°C	160°C
Vicat-temperature:	123°C	112°C
Martens-temperature:	102°C	92°C
U.L. Test:		VO

Example 9 (copolymerisation)

200 g (0.41 mol) *p*-methyltetrabromobenzylacrylate and 200 g (1.92 mol) styrene were dissolved in 800 ml toluene and after the addition of 4 g (1%) azodiisobutyronitrile, were copolymerised in a nitrogen atmosphere at 50°C for 30 hours. The resulting copolymer was precipitated from the polymer solution with an excess of methanol. After removal by suction and washing out with methanol, it was dried in a vacuum in a yield of 250 g (62.5%). The bromine content was 29.7%.

Example 10 (copolymerisation)

By the process outlined in Example 9, a copolymer was produced from 80 g (0.163 mol) *p*-methyltetrabromobenzylacrylate and 320 g (3.07 mol) styrene. The yield was 320 g (80%) and the bromine-content was 13.3%.

Example 11 (copolymerisation)

According to the procedure of Example 9, a copolymer was produced from 80 g (0.159 mol) *p*-methyltetrabromobenzylmethacrylate (formula (I), with R=CH_3) and 320 g (3.07 mol) styrene. Yield: 285 g (73%); Br-content: 14.2%.

The physical properties of the copolymers of Examples 9, 10 and 11 were as follows:

	Ex. 9	Ex. 10	Ex. 11
Softening temperature: (Kofler-block)	160°C	155°C	160°C
Vicat-temperature:	103°C	94°C	107°C
Impact strength:	10.3 KJ/m^2	10.0 KJ/m^2	-

Example 12 (copolymerisation)

An unsaturated polyester resin (UP-resin) based on 0.5 mol ethyleneglycol, 0.5 mol neopentylglycol, 0.4 mol phthalic anhydride and 0.6 mol fumaric acid, with a gel chromatrographically determined molecular weight of 3100, was dissolved to 50 parts by weight in 50 parts by weight of styrene. There were then dissolved in the styrene/UP-resin solution, 20% (based on the total) of *p*-methyltetrabromobenzyl methacrylate. After heat hardening with 2% dibenzoylperoxide-paste (50%) at 80°C, and a second cure at 135°C for 4 hours, transparent, almost colourless, 4 mm-plates were obtained which had the properties listed below. (As a contrast, the values of a styrene/UP-resin solution hardened in the same manner but without the addition of the methacrylate are also listed).

	UP-resin without addition	UP-resin/*p*-methyltetrabromo-benzylmethacrylate 80/20
Stress resistance: N/mm^2	41	39
Impact strength: KJ/m^2	5.4	8.9
Notched impact strength KJ/m^2	1.4	2.1
Resistance to bending N/mm^2	76	87
Martens-temperature: °C	98	97

Example 13 (composition)

A polyacrylate based on an acrylate corresponding to formula (I) with a bromine content of 64.6% was mixed cold in a quantity of 9%, plus 4% of Sb_2O_3, into such a quantity of polybutylene terephthalate having a reduced viscosity (ηred) of 1.48 d1/g that the total composition was 100%. The mixture was then extruded into a strand in a twin-screw extruder (of the ZDSK type manufactured by Werner & Pfleiderer) at a temperature of 260°C and the strand was granulated. Test specimens measuring 1.6 x 12.7 x 127 mm, of the type prescribed for the UL 94 fire test, were injection-moulded from the granulate. In addition, standard small test bars were injection-moulded, for measuring impact strength in accordance with DIN 53 453.

The following results were obtained:

UL 94: VO/V1 (i.e. in the fresh state: VO; after 7 days' storage at 150°C. V1)

Storage test (28 days at 150°C):	no discolouration,
	weight loss: 0.3%
	chalking: none
Impact strength according to DIN 53 453	
at 23°C:	10 specimens unbroken
at 0°C:	7 specimens unbroken
	3 specimens broken

A comparison test with pure PBT of the same viscosity gave a weight loss of 0.15% after storage for 28 days at 150°C. The results of the impact strength test according to DIN 53 453 were as follows: 10 specimens unbroken at 23°C, 10 specimens unbroken at 0°C.

Example 14 (composition)

A polyacrylate based on an acrylate corresponding to formula (I) having a bromine content of 53.0% and a chlorine content of 5.1% (produced in accordance with Example 3 but using *p*-methyl tetrabromobenzyl chloride) was mixed in a mixer with Sb_2O_3, with short glass fibres (6 mm) and with PBT granulate in accordance with the following recipe:

56% of PBT (ηred 1.53 d 1/g)
30 % of glass fbres
10 % of polyacrylate
4 % of Sb_2O_3.

After mixing, a strand granulate was produced in a single-screw extruder (Reifenhauser R 45) and this was injection-moulded into test specimens in the same way as described in Example 13.

The results of the measurements carried out in accordance with Example 13 were as follows:

UL 94: VO/VO

Storage test (28 days at 150°C):	no discolouration,
	weight loss: 0.2%
	chalking: none
Impact strength according to DIN 53 453	
at 23°C:	30.7 KJ/m^2
at 0°C:	31.2 KJ/m^2

A comparison test with pure PBT having the same viscosity and containing 30% of glass fibres showed a weight loss of 0.1% after storage for 28 days at 150°C. The impact strength according to DIN 53 453 amounted to 38.0 KJ/m^2 at 23°C and to 36.5 KJ/m^2 at 0°C.

Example 15 (composition)

Strand granulates according to Example 14 were plasticised two more times in a single-screw extruder, re-processed into strand granulates and only then injection-moulded into the form of test specimens.

Measurements of impact strength and notched impact strength showed that, contrary to expectations, the mechanical properties only minimally affected.

Despite repeated processing at elevated temperature, there was found to be no deterioration in the flameproofing effect.

Example 16 (Composition)

A standard commercially available polyethylene terephthalate (ηred 1.4 d1/g) was processed by the method described in Example 14 to form a glass-fibre-reinforced composition. Test specimens measuring 1.6 x 12.7 x 127 mm formed therefrom achieved a rating of VO/VO in the UL 94 test. No chalking occurred, even after storage for 28 days at 150°C.

Example 17 (Comparison)

A procedure was carried out as in Example 14, except that the polyacrylate was replaced by the same quantity of decabromodiphenyl ether as flameproofing agent. Processing was found to be possible, and the UL 94 fire test also produced good results. However, when the mouldings had been tempered at 150°C, a distinct chalky covering of decabromodiphenyl ether appeared on the surface after only 1 day, which covering increased as the tempering was continued.

Example 18 (composition)

12% by weight of a polyacrylate corresponding to general formula (I) (Br content 64.6%), together with 5% by weight of Sb_2O_3, both quantities based on the final composition, were worked in known manner into standard commercially available polystyrene to 100%. Test specimens were then made up from the composition for the UL 94 fire test and also the Oxygen Index Test (according to ASTM D 2863-70).

A rating of V_1 was achieved in the UL 94 test.

The Oxygen Index Test gave a value of 23.7% by volume of oxygen, as opposed to 17.1 % by volume of oxygen for the same polystyrene without the flameproofing additives according to the invention.

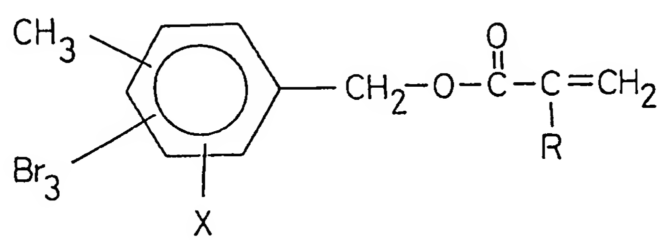
Example 19 (composition)

The polyacrylate according to Example 13 was worked in quantities of 9.5% by weight, together with 3% by weight of Sb_2O_3, into a) a polypropylene (to 100%) and b) a polyacrylate (to 100%). Similarly, a polymethacrylate corresponding to formula I containing 63.2 % by weight of bromine was processed in quantities of 11.0% by weight together with polybutylene to 100%.

In each case, good results were obtained in the UL 94 test and in the Oxygen Index Test.

CLAIMS

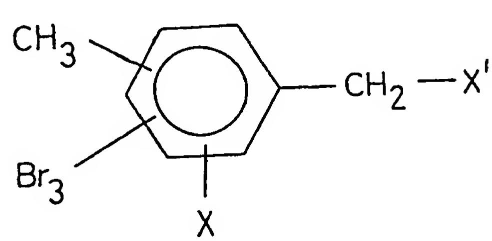
1. An ester having the general formula



(I)

in which R represents a hydrogen atom or a methyl group, and X represents bromine or chlorine.

2. An ester according to claim 1 wherein X represents a bromine atom.
3. An ester according to claim 1 wherein X represents a chlorine atom.
4. An ester according to claim 1 wherein on average the nucleus carries up to 0.3 chlorine atoms.
5. An ester according to claim 4 wherein on average the nucleus carries up to 0.1 chlorine atoms.
6. An ester according to claim 1 substantially as described in Example 1 or 2.
7. An ester according to claim 1 substantially as hereinbefore described.
8. A process for producing an ester according to claim 1 which comprises reacting a halide of general formula

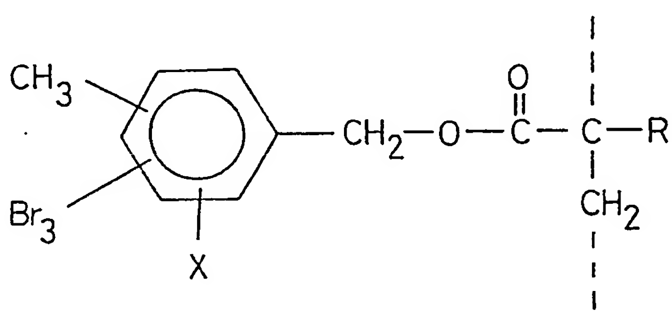


(II)

in which X′ represents a halogen atom, with an alkali metal salt of acrylic and/or methacrylic acid, to form the desired ester.

9. A process according to claim 8 wherein the salt is formed *in situ*.
10. A process according to claim 9 wherein the salt is formed *in situ* by reacting an alkali metal hydroxide, carbonate or alcoholate with acrylic or methacrylic acid.
11. A process according to claim 9 or 10 wherein the salt is formed *in situ* at a temperature of from 10 to 80°C.

12. A process according to any one of claims 8 to 11 wherein the reaction between the halide and the salt is carried out at a temperature of from 50 to 150°C.
13. A process according to claim 12 wherein the reaction between the halide and the salt is carried out at a temperature of from 80 to 130°C.
14. A process according to any one of claims 8 to 13 wherein X' represents a bromine atom.
15. A process according to any one of claims 8 to 13 wherein X' represents a chlorine atom.
16. A process according to any one of claims 8 to 15 wherein the salt is present in a stoichiometric excess.
17. A process according to claim 16 wherein the stoichiometric excess is up to 10 mol %.
18. A process according to claim 17 wherein the stoichiometric excess is up to 5 mol %.
19. A process according to any one of claims 8 to 18 when carried out in the presence of a polymerisation inhibitor.
20. A process according to claim 19 when carried out in the presence of up to 5% by weight of polymerisation inhibitor, based on the acid which is used.
21. A process according to claim 19 or 20 wherein the polymerisation inhibitor is hydroquinone.
22. A process according to any one of claims 8 to 21 when carried out in the presence of a polar organic solvent or a mixture thereof with water.
23. A process according to claim 22 wherein the organic solvent is ethylene glycol monomethyl ether.
24. A process according to any one of claims 8 to 23 which includes the additional step of separating the ester(s) of formula (I) from the product mixture.
25. A process according to claim 8 substantially as described in Example 1, 2, 3 or 4.
26. An ester of general formula (I) whenever produced by the process according to any one of claims 8 to 25.
27. A polymer which contains structural units of general formula



(III)

in which R represents a hydrogen atom or a methyl group, and X represents bromine or chlorine.
28. A polymer according to claim 27 wherein X represents a bromine atom.
29. A polymer according to claim 27 wherein X represents a chlorine atom.
30. A polymer according to claim 27 wherein on average the nucleus carries up to 0.3 chlorine atoms.
31. A polymer according to claim 30 wherein on average the nucleus carries up to 0.1 chlorine atoms.
32. A polymer according to any one of claims 27 to 31 which is a homopolymer.
33. A polymer according to claim 32 which contains from 40 to 65% by weight of halogen.
34. A polymer according to claim 33 which contains from 40 to 60% by weight of halogen.
35. A polymer according to any one of claims 27 to 31 which is a copolymer.
36. A polymer according to claim 35 which contains from 20 to 45% by weight of halogen.
37. A polymer according to claim 35 or 36 wherein in addition to the structural units of general formula (III), there are also included structural units based on an ethylenically unsaturated monomer.
38. A polymer according to claim 37 wherein the monomer comprises styrene.
39. A polymer according to claim 37 or 38 wherein the monomer comprises an acrylic or methacrylic acid ester an unsubstituted or halogen-substituted xylylene bisacrylate or bis methacrylate, acrylonitrile, butadiene or isoprene.
40. A polymer according to claim 37, 38 or 39 wherein the monomer comprises fumaric or maleic acid or an ester forming derivative thereof.
41. A polymer according to any one of claims 35 to 40 wherein in addition to the structural units of general formula (III), there are also included structural units based on an unsaturated polyester.
42. A polymer according to any one of claims 35 to 41 which contains from 10 to 20% by weight of structural units of general formula (III).
43. A polymer according to claim 42 which contains from 15 to 20% by weight of structural units of general formula (III).
44. A polymer according to claim 27 substantially as described in any one of Examples 3 to 12.
45. A polymer according to claim 27 substantially as hereinbefore described.
46. A process for producing a polymer according to claim 27 which comprises polymerising an ester of general formula (I) according to claim 1 or 26, to form the desired polymer.

47. A process according to claim 46 wherein the polymerisation is carried out in the presence of a radical former.

48. A process according to claim 47 wherein the radical former is dicumyl peroxide, dibenzoyl peroxide or azodiisobutyronitrile.

49. A process according to claim 46, 47 or 48 wherein the polymerisation is carried out at a temperature of from 0 to 150°C.

50. A process according to any one of claims 46 to 49 wherein the polymer is a copolymer and the polymerisation is carried out in the presence of a monomer which is copolymerisable with the ester of general formula (I).

51. A process accoprding to claim 50 wherein the monomer comprises styrene.

52. A process according to claim 50 or 51 wherein the monomer comprises an acrylic or methacrylic acid ester, an unsubstituted or halogen substituted xylylene bis acrylate or bis methacrylate, acrylonitrile, butadiene or isoprene.

53. A process according to claim 50, 51 or 52 wherein the monomer comprises fumaric or maleic acid or an ester forming derivative thereof.

54. A process according to any one of claims 46 to 53 wherein the polymer is a copolymer and the polymerisation is carred out in the presence of an unsaturated polyester which is copolymerisable with the ester of general formula (I).

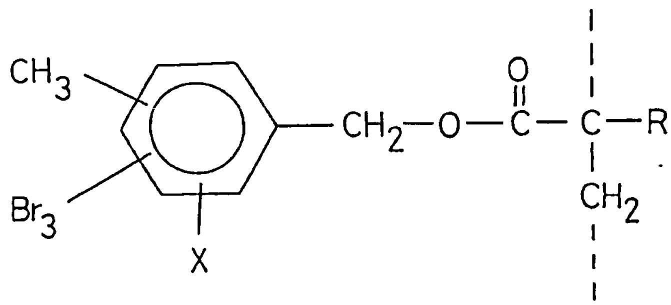
55. A process according to any one of claims 46 to 54 wherein the ester of general formula (I) is a component of the product mixture formed by the process according to any one of claims 8 to 25.

56. A process according to any one of claims 46 to 55 wherein the ester of general formula (I) is produced in accordance with the process of claim 8 and is polymerised immediately thereafter.

57. A process according to claim 46 substantially as described in any one of Examples 3 to 12.

58. A polymer whenever produced by the process according to any one of claims 46 to 57.

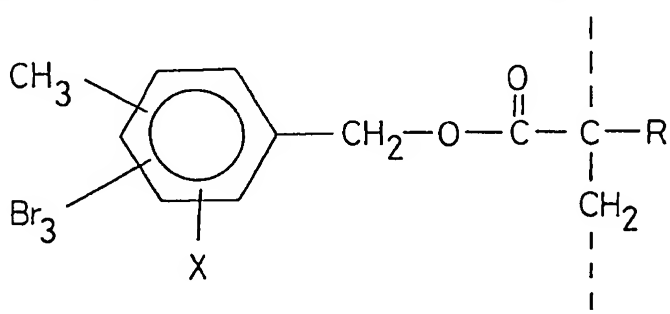
59. A plastics composition comprises a polymeric material and, as flameproofing agent therefor, a polymer containing structural units of general formula



(III)

in which R represents a hydrogen atom or a methyl group, and X represents bromine or chlorine.

60. A plastics composition which comprises a polymeric material and, in physical admixture therewith as flameproofing agent, a polymer containing structural units of general formula



(III)

in which R represents a hydrogen atom or a methyl group, and X represents bromine or chlorine.

61. A composition according to claim 59 or 60 wherein X represents a bromine atom.

62. A composition according to claim 59 or 60 wherein X represents a chlorine atom.

63. A composition according to claim 59 or 60 wherein on average the nucleus carries up to 0.3 chlorine atoms.

64. A composition according to claim 63 wherein on average the nucleus carries up to 0.1 chlorine atoms.

65. A composition according to any one of claims 59 to 64 wherein the polymeric material is thermoplastic.

66. A composition according to any one of claims 59 to 64 wherein the polymeric material is a high melting plastics material.

67. A composition according to any one of claims 59 to 64 wherein the polymeric material comprises a polyester.

68. A composition according to claim 67 wherein the polyester is polyethylene terephthalate or polybutylene terephthalate.

69. A composition according to any one of claims 59 to 64 wherein the polymeric material comprises a polyolefin.

70. A composition according to claim 69 wherein the polyolefin is polyethylene, polypropylene or polybutylene.

71. A composition according to any one of claims 59 64 wherein the polymeric material comprises a polyacrylate or polymethacrylate.

72. A composition according to any one of claims 59 to 64 wherein the polymeric material comprises polyacrylonitrile.

73. A composition according to any one of claims 59 to 64 wherein the polymeric material comprises polystyrene.

74. A composition according to any one of claims 59 to 64 wherein the polymeric material comprises a polyether, polyacetal, polysulphone, polyimide, polycarbonate, polyphenylene sulphide or polyaryl ester.

75. A composition according to any one of claims 59 to 74 which includes from 5 to 20% by weight of the polymer.

76. A composition according to claim 75 which includes from 7 to 12% by weight of the polymer.

77. A composition according to any one of claims 59 to 76 which additionally includes a substance which acts synergistically with the flameproofing polymer.

78. A composition according to claim 77 which includes from 2 to 12% by weight of the substance.

79. A composition according to claim 78 which includes from 4 to 7% by weight of the substance.

80. A composition according to claim 77, 78 or 79 wherein the substance is a compound of antimony or of boron.

81. A composition according to claim 80 wherein the substance is antimony trioxide.

82. A composition according to any one of claims 59 to 81 which additionally includes a filler and/or a reinforcing material.

83. A composition according to claim 82 which includes from 2 to 60% by weight of filler and/or reinforcing material.

84. A composition according to claim 83 which includes from 10 to 40% by weight of filler and/or reinforcing material.

85. A composition according to claim 82, 83 or 84 wherein the filler and/or reinforcing material comprises glass fibres.

86. A composition according to claim 59 or 60 substantially as described in Example 13, 14, 15, 16, 18 or 19.

87. A process for producing a composition according to claim 59 or 60 which comprises admixing the polymer and the polymeric material to form the desired composition.

88. A process according to claim 87 substantially as described in Example 13, 14, 15, 16, 18 or 19.

89. A composition whenever produced by the process according to claim 87 or 88.

90. An article when formed from a polymer according to any one of claims 27 to 45 and 58 or a composition according to any one of claims 59 to 86 and 89.

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